

The Conductivities, Temperature Coefficients of Conductivity and Dissociation of Certain Electrolytes from 0° to 35° , and of Certain Other Electrolytes from 35° to 65° .

DISSERTATION.

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF THE JOHNS HOPKINS UNIVERSITY IN CONFORMITY WITH THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY.

BY

HENRY HALLOCK HOSFORD.

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THE CONDUCTIVITIES, TEMPERATURE COEFFICIENTS OF CONDUCTIVITY AND DISSOCIATION OF CERTAIN ELECTROLYTES

HISTORICAL REVIEW

Volta, at the end of the eighteenth century, distinguished two classes of conductors of the then recently discovered galvanism. The first class comprised those substances, such as metals, which conduct without chemical change; while conductors of the second class were decomposed by the passage of the current. A few years later, by electrolyzing conductors of the second class, Davy isolated the previously unknown metals of the alkalis and the alkaline earths. Faraday,¹ in 1832, published his laws showing the relation between the amount of electricity passed through the electrolyte and the amount of the electrolyte decomposed.

Measurements of the resistance of solutions of electrolytes were soon made by many investigators. Of these early researches those of Hankel,² Becquerel,³ Horsford,⁴ Wiedeman,⁵ Becker,⁶ and Beetz⁷ may be especially noted. Brief discussions of these and other investigations can be found in Wiedemann's book.⁸

The earlier methods were very imperfect. The continuous current was used, causing polarization of the electrodes, except in some special cases, as when the metal of the salt was used for the electrodes. The standard method now used practically eliminates polarization by using the alternating current. This method was first developed and used by Kohlrausch and his coworkers in a series of researches⁹ that were far more comprehensive than any preceding investigations.

¹ Exp. Researches, III, Ser. No. 373 (1832).

² Pogg. Ann., 69, 255 (1846).

³ Ann. chim. phys., [3] 17, 267 (1846).

⁴ Pogg. Ann., 70, 238 (1847).

⁵ Ibid., 99, 225 (1856).

⁶ Ann. Chem. (Liebig), 73, 1 (1850); 75, 94 (1851).

⁷ Pogg. Ann., 117, 1 (1862).

⁸ G. Wiedemann: Die Lehre von der Elektrizität, Band I (Braunschweig, 1882).

⁹ For brief discussions and references to original publications see Wiedemann:

The dissociation theory of Arrhenius¹ imparted new life to conductivity measurements of electrolytes as affording a basis for the accurate determination of the degree of ionization.

Following Kohlrausch, many investigations in this field have been carried out, but in most cases with some special object in view which has limited the scope of the work. The researches were concerned with a few substances only, or were confined to a narrow range of temperature and concentration.

PURPOSE OF THIS INVESTIGATION

It has seemed desirable to secure conductivity data relative to all the substances in more common use by the chemist, and under the conditions of temperature and dilution at which they are usually employed in chemical work. With this end in view, a systematic study of the electrical conductivities and allied relations of acids, bases and salts in aqueous as well as in nonaqueous solutions, and at various temperatures and concentrations, has been in progress in this laboratory for ten years. Six papers¹ dealing solely with aqueous solutions have been published and other investigations are in progress.

The work herein described was undertaken as a continuation of that already carried out on the general problem. It includes the determination of the electrical conductivities, temperature coefficients of conductivity and percentage dissociation of a number of inorganic salts at dilutions ranging from $N/2$ to $N/4096$. Some of the measurements were made over a range of temperature from 0° to 35° , and a part from 35° to 65° .

PREPARATION OF MATERIAL

The salts used were the purest available. In nearly all cases Kahlbaum's chemicals were employed. These were recrystallized from one to five times, the final crystallizations in all cases being made from water of special purity or so-called "conductivity water." Any deviations from this general

¹ Z. physik. Chem., **1**, 631 (1881). Scientific Memoirs, Series IV, p. 47.

² Jones and Douglas: Am. Chem. J., **26**, 428 (1901). Jones and West: *Ibid.*, **34**, 357 (1905). Jones and Jacobson: *Ibid.*, **40**, 355 (1908). Clover and Jones: *Ibid.*, **43**, 187 (1910). White and Jones: *Ibid.*, **44**, 159 (1910). West and Jones: *Ibid.*, **44**, 508 (1910).

procedure are stated in connection with the experimental data under each salt.

The water used in making up the solutions was prepared by a modification of the method of Jones and Mackay,¹ i. e., by subjecting the distilled water of the laboratory to three additional distillations: first in the presence of potassium dichromate and sulphuric acid to oxidize organic matter and retain ammonia, and twice with barium hydroxide to absorb carbon dioxide. The conductivity of such water varies from 1.0 to 1.5×10^{-6} . The correction of the molecular conductivity due to this cause is negligible in the greater concentrations, but was calculated and applied to the conductivity values obtained for the dilute solutions.

APPARATUS AND METHOD

The Kohlrausch method was used in this investigation. In the work from 35° to 65° a slide-wire bridge of the usual type was employed, while measurements from 0° to 35° were made by means of an improved slide-wire bridge made by Leeds and Northrup, the wire being about five meters long. The bridges and resistance coils were standardized by Leeds and Northrup and also by means of resistances which had been corrected by the U. S. Bureau of Standards.

The conductivity cells were of the type used and described by Clover and Jones² and Jones and West.³ The constants of these cells were determined at short intervals. In connection with the work from 0° to 35° the following method of determining the constants was employed. A 0.02 N solution of carefully purified potassium chloride was prepared, using water of special purity. The molecular conductivity of this solution at 25° was assumed to have Kohlrausch's value of 129.7 , and this solution was used to determine the constants of the cells designed for concentrated solutions. A 0.002 N solution of potassium chloride was also prepared, and its molecular conductivity found by means of a cell whose constant had been determined as explained above. This 0.002 N

¹ *Z. physik. Chem.*, **14**, 317 (1894). *Am. Chem. J.*, **19**, 91 (1897).

² *Am. Chem. J.*, **43**, 192 (1910).

³ *Ibid.*, **44**, 510 (1910).

solution was then used in finding the constants of the cells intended for the more dilute solutions.

In connection with the work from 0° to 35° , a slightly different plan was adopted. Solutions of potassium chloride of 0.02 N and 0.002 N concentration were prepared and used as described; but a fixed value of 136.5 at 25° was taken for the molecular conductivity of the 0.002 N solution. This value is based on repeated measurements made in this laboratory.

So far as possible the initial or mother solution of each salt was prepared by direct weighing of the properly purified substance. If this was impracticable a mother solution of convenient strength was made up and standardized by analysis. From the mother solution the various concentrations were prepared by dilution. In the case of the work from 0° to 35° , solutions were made up at 20° and were used without corrections at the various temperatures at which measurements were made, the correction being less than the known experimental error. When working from 35° to 65° solutions were prepared at 50° , and a factor was employed in the reduction of all measurements made at 35° and 65° to correct for the change in concentration due to change in volume. The correction factor for the molecular conductivity of solutions made at 50° and used at 35° is 0.994; for those made at 50° and used at 65° the value is 1.0076. The burettes and measuring flasks used in making up solutions were carefully calibrated for the temperature at which they were to be used.

For the work at 0° an ice bath was employed in which the cells were supported so as to be immersed as deeply as possible in the crushed ice and water. A shallow vessel filled with ice and water covered the ice baths when in use. Connections were made through openings closed with perforated stoppers carrying the conducting wires. The baths for higher temperatures were properly sheathed with asbestos cement, and in the case of the 50° and 65° baths efficient covers were provided to retain the heat. Hot-air engines were used to stir the baths. It was found easy to keep the temperature of the baths constant to within $0^{\circ}.02$ or $0^{\circ}.03$ by hand regulation, and this method was adopted.

From two to four independent measurements of the conductivity were made for each concentration at each temperature. If there was not close agreement in the results, or if any abnormally large errors were suspected, the measurements were repeated. So far as possible my results were compared with those obtained by other workers. In most cases there is reasonable agreement. When wide discrepancies appeared my work was duplicated.

Concentrations are indicated under the heading *V*, or the number of liters which would contain one gram-molecular weight of the salt. Molecular conductivities are expressed in Siemens' units. The temperature coefficients and dissociation were calculated in the usual way. On account of hydrolysis or other causes, the maximum value of the molecular conductivity (μ_{∞}) was not found for certain salts at the greatest dilution worked with. In such cases the dissociation was not calculated.

Ammonium Aluminium Sulphate, $\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$

The mother solution was standardized by determining aluminium as aluminium oxide.

Table I.—Molecular Conductivity

<i>V</i>	0°	12°.5	25°	35°
8	80.0	110.9	143.1	168.8
32	102.5	143.1	185.5	220.4
128	130.1	182.7	238.8	284.8
512	162.2	230.9	304.5	365.9
1024	181.0	257.5	342.4	415.1
2048	201.8	288.2	386.4	485.8
4096	224.1	322.8	437.6	540.3

Table II.—Temperature Coefficients

<i>V</i>	0°–12°.5		12°.5–25°		25°–35°	
	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
8	2.47	3.09	2.58	2.33	2.57	1.80
32	3.25	3.17	3.39	2.37	3.49	1.88
128	4.21	3.24	4.49	2.46	4.60	1.93
512	5.50	3.39	5.89	2.55	6.14	2.02
1024	6.12	3.38	6.79	2.64	7.27	2.12
2048	6.91	3.42	7.86	2.73	9.94	2.57
4096	7.90	3.53	8.38	2.60	10.27	2.35

Ammonium Chromium Sulphate (Violet Variety).

The mother solution was standardized in the same manner as in the case of the potassium salt.

Table III.—Molecular Conductivity

V	0°	12°.5	25°	35°
8	77.5	106.4	137.3	162.7
16	88.9	123.2	159.5	188.3
32	100.8	140.3	182.2	216.0
128	129.5	183.0	240.2	285.9
512	165.5	238.0	321.0	385.9
1024	187.0	272.0	372.0	455.7
2048	211.9	310.7	428.5	530.0
4096	240.7	355.6	492.2	617.0

Table IV.—Temperature Coefficients

V	0°-12°.5		12°.5-25°		25°-35°	
	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
8	2.31	2.98	2.47	2.32	2.54	1.85
16	2.74	3.08	2.90	2.35	2.88	1.81
32	3.16	3.14	3.35	2.39	3.38	1.86
128	4.28	3.31	4.57	2.50	4.57	1.90
512	5.80	3.51	6.64	2.79	6.49	2.02
1024	6.80	3.64	8.00	2.94	8.37	2.25
2048	7.90	3.73	9.40	3.03	10.15	2.37
4096	9.19	3.82	10.93	3.07	12.48	2.54

Ammonium Chromium Sulphate (Green Variety)

The mother solution was prepared by heating a portion of the mother solution of the violet variety to 70° for about seven hours in a stoppered bottle.

Table V.—Molecular Conductivity

V	0°	12°.5	25°	35°
8	103.6	133.2	162.9	185.3
16	119.7	155.4	190.6	219.3
32	136.4	178.2	220.8	255.1
128	172.3	228.4	288.1	336.4
512	202.6	274.4	355.7	423.2
1024	215.6	294.2	386.2	471.2
2048	222.0	313.5	414.0	518.4
4096	234.4	328.4	458.1	593.8

Table VI.—Temperature Coefficients

V	0°-12°.5		12°.5-25°		25°-35°	
	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
8	2.37	2.29	2.38	1.79	2.24	1.38
16	2.70	2.26	2.82	1.82	2.87	1.51
32	3.34	2.45	3.41	1.91	3.43	1.55
128	4.49	2.61	4.78	2.09	4.83	1.68
512	5.74	2.83	6.50	2.37	6.75	1.90
1024	6.29	2.92	7.36	2.50	8.50	2.20
2048	7.32	3.37	8.04	2.57	10.44	2.52
4096	7.52	3.21	10.38	3.16	13.57	2.96

Ammonium Copper Sulphate, (NH₄)₂Cu(SO₄)₂·6H₂O

The mother solution was standardized by determining the sulphuric acid as barium sulphate, and the copper was also determined as copper oxide.

Table VII.—Molecular Conductivity

V	0°	12°.5	25°	35°
4	106.3	146.6	190.4	225.7
8	122.7	169.9	220.7	262.2
32	153.5	213.8	280.2	334.3
128	187.8	262.4	346.7	412.6
512	221.6	312.1	411.7	495.7
1024	236.0	333.5	442.6	532.5
2048	246.4	347.9	463.6	560.0
4096	259.4	367.3	494.0	597.3

Table VIII.—Temperature Coefficients

V	0°-12°.5		12°.5-25°		25°-35°	
	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
4	3.22	3.03	3.50	2.39	3.53	1.85
8	3.78	3.08	4.06	2.39	4.15	1.88
32	4.82	3.14	5.31	2.48	5.41	1.93
128	5.97	3.18	6.74	2.57	6.59	1.90
512	7.24	3.27	7.97	2.55	8.40	2.04
1024	7.80	3.31	8.73	2.62	8.99	2.03
2048	8.12	3.30	9.26	2.66	9.64	2.08
4096	8.63	3.33	10.14	2.76	10.33	2.09

Sodium Ferrocyanide, $\text{Na}_4\text{Fe}(\text{CN})_6 \cdot 12\text{H}_2\text{O}$

The mother solution was made up by direct weighing of the anhydrous salt.

Table IX.—Molecular Conductivity

V	0°	12°.5	25°	35°
8	136.7	194.9	259.2	313.4
16	151.3	215.5	287.0	347.7
32	167.1	238.5	318.5	386.2
128	203.5	289.6	385.9	464.5
512	234.2	334.1	446.4	543.2
1024	253.4	361.7	482.4	581.2
2048	266.4	380.3	504.0	612.0
4096	275.7	398.1	527.1	632.2

Table X.—Temperature Coefficients

V	0°–12°.5		12°.5–25°		25°–35°	
	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
8	4.66	3.41	5.14	2.64	5.42	2.09
16	5.14	3.40	5.72	2.65	6.07	2.12
32	5.71	3.42	6.40	2.68	6.77	2.13
128	6.89	3.39	7.70	2.66	7.86	2.04
512	7.99	3.41	8.98	2.69	9.68	2.17
1024	8.66	3.42	9.66	2.67	9.88	2.05
2048	9.11	3.42	9.90	2.60	10.80	2.14
4096	9.79	3.55	10.32	2.59	10.51	2.00

Table XI.—Percentage Dissociation

V	0°	12°.5	25°	35°
8	49.58	48.96	49.18	49.57
16	54.88	54.13	54.45	55.00
32	60.61	59.91	60.43	61.09
128	73.81	72.74	73.21	73.47
512	84.95	83.92	84.69	85.92
1024	91.91	90.86	91.52	91.93
2048	96.63	95.53	95.62	96.81
4096	100.00	100.00	100.00	100.00

Potassium Sodium Sulphate, KNaSO_4

The mother solution was standardized by determining sulphuric acid as barium sulphate.

Table XII.—Molecular Conductivity

V	0°	12°.5	25°	35°
4	88.4	122.5	159.0	189.6
8	96.1	146.6	170.6	209.1
32	113.0	158.1	207.2	249.7
128	128.8	179.0	236.1	284.5
512	135.6	189.6	250.8	301.0
1024	140.8	197.1	259.2	313.2
2048	140.9	198.2	261.4	316.2
4096	144.3	202.6	267.6	322.1

Table XIII.—Temperature Coefficients

V	0°-12°.5		12°.5-25°		25°-35°	
	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
4	2.73	3.09	2.92	2.38	3.06	1.92
8	4.04	4.30	1.92	1.30	3.85	1.79
32	3.68	3.26	3.93	2.49	4.25	2.05
128	4.02	3.12	4.57	2.55	4.84	2.05
512	4.32	3.19	4.90	2.58	5.02	2.00
1024	4.50	3.20	4.97	2.52	5.40	2.08
2048	4.58	3.25	5.06	2.55	5.48	2.10
4096	4.66	3.23	5.20	2.56	5.45	2.04

Table XIV.—Percentage Dissociation

V	0°	12°.5	25°	35°
4	61.26	60.46	59.42	58.88
8	66.60	72.36	63.75	64.93
32	78.31	78.03	77.43	77.54
128	89.26	88.35	88.23	88.35
512	93.97	93.58	93.72	93.47
1024	97.57	97.28	96.86	97.26
2048	97.64	97.83	97.68	98.19
4096	100.00	100.00	100.00	100.00

Potassium Aluminium Sulphate, $KAl(SO_4)_2 \cdot 12H_2O$

The mother solution was standardized by determining aluminium as aluminium oxide.

Table XV.—Molecular Conductivity

V	0°	12°.5	25°	35°
8	78.9	108.9	140.3	165.3
32	101.2	140.8	182.2	215.7
128	127.6	177.7	232.9	283.7
512	158.8	223.7	294.9	358.3
1024	177.8	250.5	332.7	402.8
2048	197.5	281.8	378.4	470.0
4096	218.8	314.7	425.5	528.8

Table XVI.—Temperature Coefficients

V	0°-12°.5		12°.5-25°		25°-35°	
	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
8	2.40	3.04	2.51	2.30	2.50	1.78
32	3.17	3.13	3.31	2.35	3.35	1.84
128	4.01	3.14	4.42	2.49	5.08	2.18
512	5.19	3.27	5.69	2.54	6.34	2.15
1024	5.81	3.27	6.57	2.62	7.01	2.11
2048	6.74	3.41	7.73	2.74	9.16	2.42
4096	7.67	3.51	8.86	2.82	10.33	2.43

Potassium Nickel Sulphate, $K_2Ni(SO_4)_2 \cdot 6H_2O$

The mother solution was standardized by determining sulphuric acid as barium sulphate and also by determining nickel as oxide.

Table XVII.—Molecular Conductivity

V	0°	12°.5	25°	35°
8	122.6	170.7	221.9	265.3
32	155.4	217.0	283.8	339.7
128	187.5	263.0	344.8	414.1
512	219.6	309.3	407.7	490.7
1024	235.5	331.2	437.1	527.1
2048	249.5	349.9	463.0	560.1
4096	260.8	367.9	487.4	588.1

Table XVIII.—Temperature Coefficients

V	0°-12°.5		12°.5-25°		25°-35°	
	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
8	3.85	3.14	4.10	2.40	4.34	1.96
32	4.93	3.17	5.32	2.45	5.59	1.97
128	6.04	3.22	6.54	2.48	6.93	2.01
512	7.18	3.27	7.87	2.54	8.30	2.04
1024	7.66	3.25	8.47	2.56	9.00	2.06
2048	8.03	3.22	9.05	2.59	9.71	2.09
4096	8.57	3.29	9.56	2.60	10.07	2.07

Table XIX.—Percentage Dissociation

V	0°	12°.5	25°	35°
8	47.01	46.40	45.53	45.11
32	59.59	58.98	58.23	57.76
128	71.89	71.49	70.74	70.41
512	84.20	84.07	83.65	83.44
1024	90.30	90.02	89.68	89.63
2048	95.67	95.11	94.99	95.24
4096	100.00	100.00	100.00	100.00

Potassium Chromium Sulphate (Violet Variety),
 $\text{KCr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$

The mother solution was standardized by determining chromium as chromic oxide and also by determining sulphuric acid as barium sulphate.

Table XX.—Molecular Conductivity

V	0°	12°.5	25°	35°
8	75.8	105.0	135.3	159.4
16	87.3	121.2	157.3	185.3
32	99.0	138.1	179.6	211.3
128	127.0	179.5	236.7	279.9
512	161.1	232.0	311.5	374.5
1024	186.6	271.6	369.6	443.8
2048	213.3	314.2	428.8	520.6
4096	245.8	364.8	500.1	613.9

Table XXI.—Temperature Coefficients

V	0°-12°.5		12°.5-25°		25°-35°	
	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
8	2.34	3.09	2.42	2.31	2.41	1.78
16	2.71	3.10	2.89	2.38	2.80	1.78
32	3.13	3.16	3.32	2.40	3.17	1.77
128	4.20	3.31	4.58	2.55	4.32	1.82
512	5.67	3.52	6.36	2.74	6.30	2.02
1024	6.80	3.64	7.84	2.89	7.42	2.01
2048	8.07	3.78	9.17	2.92	9.18	2.14
4096	9.52	3.87	10.82	2.97	11.38	2.28

Potassium Chromium Sulphate (Green Variety)

The mother solution was prepared by heating a portion of the mother solution of the violet variety to 70° for about seven hours in a stoppered bottle.

Table XXII.—Molecular Conductivity

V	0°	12°.5	25°	35°
8	101.0	130.1	158.4	179.6
16	119.3	154.0	188.1	213.2
32	137.8	179.3	219.5	249.3
128	177.7	234.4	290.6	333.5
512	210.9	283.5	359.1	426.6
1024	229.7	310.9	399.6	479.0
2048	247.0	339.5	441.3	539.1
4096	273.1	379.4	500.3	616.2

Table XXIII.—Temperature Coefficients

V	0°–12°.5		12°.5–25°		25°–35°	
	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
8	2.33	2.31	2.26	1.74	2.12	1.34
16	2.78	2.33	2.73	1.77	2.51	1.33
32	3.32	2.41	3.22	1.80	2.98	1.36
128	4.54	2.55	4.50	1.92	4.29	1.48
512	5.81	2.76	6.05	2.13	6.75	1.88
1024	6.50	2.83	7.10	2.28	7.94	1.99
2048	7.40	3.00	8.14	2.40	9.78	2.22
4096	8.50	3.11	9.67	2.55	11.59	2.32

Calcium Formate, $\text{Ca}(\text{OOCH})_2$

The mother solution was standardized by determining calcium as the sulphate.

Table XXIV.—Molecular Conductivity

V	0°	12°.5	25°	35°
4	58.4	81.7	107.1	128.6
8	67.2	94.4	124.5	149.7
32	81.4	115.3	153.1	184.7
128	92.2	131.2	174.3	211.6
512	95.7	135.5	181.9	223.5
2048	101.4	144.6	190.4	230.6
4096	101.3	145.4	190.6	229.2

Table XXV.—Temperature Coefficients

V	0°–12°.5		12°.5–25°		25°–35°	
	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
4	1.86	3.19	2.03	2.49	2.15	2.01
8	2.18	3.24	2.41	2.55	2.52	2.02
32	2.70	3.32	3.02	2.62	3.16	2.06
128	3.12	3.38	3.45	2.63	3.73	2.14
512	3.18	3.32	3.71	2.74	4.16	2.29
2048	3.46	3.41	3.66	2.53	4.02	2.11
4096	3.53	3.48	3.62	2.49	3.86	2.03

Table XXVI.—Percentage Dissociation

V	0°	12°.5	25°	35°
4	57.65	56.19	56.19	56.11
8	66.34	64.92	65.32	65.31
32	80.36	79.30	80.33	80.58
128	91.02	90.23	91.45	92.32
512	94.47	93.19	95.44	97.51
2048	100.00	99.45	99.89	100.00
4096		100.00	100.00	

Calcium Chromate, CaCrO₄

The mother solution was standardized by titrating with ferrous ammonium alum.

Table XXVII.—Molecular Conductivity

V	0°	12°.5	25°	35°
8	57.7	80.9	105.8	125.4
16	64.6	90.4	118.5	140.9
32	72.2	101.4	133.1	158.2
128	91.2	126.9	167.5	200.8
512	106.7	150.0	198.7	239.5
1024	111.6	157.3	208.8	253.3
2048	114.4	160.8	214.0	264.0
4096	116.1	162.5	216.1	261.6

Table XXVIII.—Temperature Coefficients

V	0°–12°.5		12°.5–25°		25°–35°	
	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
8	1.85	3.21	1.99	2.46	1.96	1.85
16	2.06	3.19	2.25	2.49	2.24	1.89
32	2.33	3.23	2.54	2.51	2.51	1.89
128	2.86	3.14	3.25	2.56	3.33	1.99
512	3.46	3.24	3.90	2.60	4.08	2.05
1024	3.66	3.28	4.12	2.62	4.45	2.13
2048	3.71	3.24	4.26	2.65	5.00	2.34
4096	3.71	3.20	4.29	2.64	4.55	2.11

Table XXIX—Percentage Dissociation

V	0°	12°.5	25°	35°
8	49.70	49.78	48.96	47.94
16	55.64	55.63	54.85	53.86
32	62.19	62.40	61.59	60.47
128	78.55	78.09	77.51	76.76
512	91.90	92.31	91.95	91.55
1024	96.12	96.80	96.62	96.83
2048	98.54	98.95	99.03	100.00
4096	100.00	100.00	100.00	

Zinc Nitrate, Zn(NO₃)₂.6H₂O

The mother solution was standardized by determining zinc as zinc oxide.

Table XXX.—Molecular Conductivity

V	0°	12°.5	25°	35°
4	80.6	110.8	146.6	171.2
8	87.6	121.2	157.2	188.5
32	100.0	139.2	182.1	219.0
128	110.4	154.1	202.6	243.5
512	114.1	164.9	210.1	254.3
1024	117.1	165.0	216.6	261.3
2048	120.4	169.2	222.4	270.2
4096	124.4	175.0	229.1	279.4

Table XXXI.—Temperature Coefficients

V	0°-12°.5		12°.5-25°		25°-35°	
	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
4	2.42	3.00	2.86	2.58	2.46	1.68
8	2.69	3.07	2.88	2.38	3.13	1.99
32	3.34	3.34	3.43	2.46	3.69	2.03
128	3.50	3.17	3.88	2.52	4.09	2.02
512	4.06	3.56	3.62	2.20	4.42	2.10
1024	3.83	3.27	4.13	2.50	4.47	2.06
2048	3.90	3.24	4.26	2.52	4.78	2.15
4096	4.05	3.26	4.33	2.47	5.03	2.20

Table XXXII.—Percentage Dissociation

V	0°	12°.5	25°	35°
4	64.79	63.31	63.99	61.27
8	70.42	69.26	68.62	67.47
32	80.39	79.54	79.48	78.38
128	88.75	88.06	88.43	87.15
512	91.92	94.23	91.71	91.02
1024	94.13	94.29	94.54	93.52
2048	96.78	96.68	97.07	96.71
4096	100.00	100.00	100.00	100.00

Zinc Acetate, $\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2$

The mother solution was standardized by determining zinc as zinc oxide.

Table XXXIII.—Molecular Conductivity

V	0°	12°.5	25°	35°
4	27.8	38.0	48.0	55.0
8	37.7	52.2	66.6	77.2
32	55.5	78.6	103.0	122.4
128	70.0	100.7	134.2	162.1
512	78.6	113.7	153.2	185.5
1024	79.9	116.1	156.7	191.6
2048	83.2	120.8	163.2	200.1
4096	83.8	121.3	163.4	201.1

Table XXXIV.—*Temperature Coefficients*

V	0°–12°.5		12°.5–25°		25°–35°	
	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
4	0.81	2.91	0.80	2.11	0.70	1.46
8	1.16	3.08	1.15	2.20	1.06	1.59
32	1.85	3.33	1.95	2.48	1.94	1.88
128	2.45	3.50	2.68	2.66	2.79	2.08
512	2.81	3.58	3.16	2.78	3.23	2.11
1024	2.90	3.63	3.25	2.79	3.49	2.23
2048	3.01	3.61	3.39	2.81	3.69	2.26
4096	3.00	3.58	3.37	2.78	3.77	2.31

Table XXXV.—*Percentage Dissociation*

V	0°	12°.5	25°	35°
4	33.17	31.33	29.38	27.35
8	44.99	43.03	40.76	38.39
32	66.23	64.80	63.03	60.87
128	83.53	83.02	82.13	80.61
512	93.79	93.73	93.76	92.24
1024	95.34	95.71	95.90	95.28
2048	99.28	99.59	99.86	99.50
4096	100.00	100.00	100.00	100.00

Lead Acetate, $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$

The mother solution was standardized by determining lead as lead sulphate.

Table XXXVI.—*Molecular Conductivity*

V	0°	12°.5	25°	35°
4	11.2	16.4	22.1	27.0
8	16.0	23.3	31.2	37.8
32	28.8	41.4	54.9	66.2
128	46.4	66.3	87.1	104.2
512	65.3	92.7	123.1	146.2
1024	74.5	108.2	139.1	167.2
2048	84.3	119.4	156.8	189.1
4096	87.8	124.6	165.5	198.7

Table XXXVII.—Temperature Coefficients

V	0°-12°.5		12°.5-25°		25°-35°	
	Cond. units	Per cent.	Cond. units	Per cent.	Cond. units	Per cent.
4	0.41	3.66	0.46	2.81	0.49	2.22
8	0.58	3.63	0.63	2.70	0.66	2.12
32	1.01	3.50	1.08	2.61	1.13	2.06
128	1.59	3.42	1.66	2.50	1.71	1.96
512	2.19	3.35	2.43	2.62	2.31	1.88
1024	2.70	3.62	2.47	2.28	2.81	2.02
2048	2.81	3.34	2.99	2.50	3.23	2.06
4096	2.94	3.35	3.27	2.62	3.32	2.15

Table XXXVIII.—Percentage Dissociation

V	0°	12°.5	25°	35°
4	12.76	13.16	13.35	13.59
8	18.22	18.70	18.85	19.02
32	32.80	33.23	33.17	33.32
128	52.85	53.21	52.63	52.44
512	74.38	74.40	74.38	73.58
1024	84.86	86.84	84.05	84.15
2048	96.02	95.83	94.74	95.17
4096	100.00	100.00	100.00	100.00

Ammonium Aluminium Sulphate, $\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$

The mother solution was standardized by determining sulphuric acid as barium sulphate.

Table XXXIX.—Molecular Conductivity

V	35°	50°	65°
8	168.8	203.5	236.5
16	202.3	247.5	288.0
64	261.5	325.8	384.8
128	284.8	347.5	426.3
512	365.9	477.5	573.5
2048	485.8	643.1	831.5

Table XL.—Temperature Coefficients

V	35°-50°		50°-65°	
	Cond. units.	Per cent.	Cond. units	Per cent.
8	2.31	1.37	2.20	1.08
16	3.01	1.48	2.70	1.09
64	4.29	1.64	3.93	1.21
128	4.18	1.47	5.25	1.51
512	7.44	2.03	6.40	1.34
2048	10.49	2.16	12.56	1.95

Disodium Phosphate, $\text{HNa}_2\text{PO}_4 \cdot 12\text{H}_2\text{O}$

The mother solution was standardized by determining the phosphoric acid as magnesium pyrophosphate.

Table XLI.—Molecular Conductivity and Dissociation

V	35°		50°		65°	
	μ_v	α	μ_v	α	μ_v	α
8	141.8	61.8	184.1	61.5	228.0	60.6
32	176.8	77.0	228.2	76.3	287.9	76.6
128	206.5	90.9	269.0	89.8	334.4	88.9
512	224.3	97.8	292.7	97.8	376.1	100.0
2048	229.5	100.0	299.3	100.0	(355.4)	

Table XLII.—Temperature Coefficients

V	35°–50°		50°–65°	
	Cond. units	Per cent.	Cond. units	Per cent.
8	2.82	1.99	2.93	1.59
32	3.43	1.94	3.98	1.74
128	4.17	2.02	4.36	1.62
512	4.56	2.03	5.56	1.90
2048	4.65	2.03	4.65	...

Sodium Tetraborate, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O}$

The mother solution was standardized as the anhydrous salt.

Table XLIII.—Molecular Conductivity and Dissociation

V	35°		50°		65°	
	μ_v	α	μ_v	α	μ_v	α
16	141.3	70.9	182.8	67.6	231.3	64.4
32	157.1	78.8	204.0	75.5	256.2	71.3
128	172.4	86.5	224.1	82.9	281.6	78.4
512	186.7	93.6	247.8	91.7	316.7	88.1
2048	199.4	100.0	270.3	100.0	359.3	100.0

Table XLIV.—Temperature Coefficients

V	35°–50°		50°–65°	
	Cond. units	Per cent.	Cond. units	Per cent.
16	2.77	1.96	3.23	1.76
32	3.13	1.99	3.48	1.71
128	3.45	2.00	3.83	1.71
512	4.01	2.15	4.59	1.85
2048	4.73	2.37	5.93	2.19

Potassium Aluminium Sulphate, $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$

The mother solution was standardized by determining sulphuric acid as barium sulphate.

Table XLV.—Molecular Conductivity

V	35°	50°	65°
4	142.3	172.5	196.1
8	165.3	207.5	240.6
32	215.7	255.1	317.4
128	283.7	356.9	426.2
512	358.3	446.9	557.1
2048	470.0	626.4	796.4

Table XLVI.—Temperature Coefficients

V	35°–50°		50°–65°	
	Cond. units	Per cent.	Cond. units	Per cent.
4	2.01	1.41	1.57	0.87
8	2.81	1.70	2.21	1.06
32	2.63	1.22	4.15	1.63
128	4.88	1.72	4.62	1.29
512	5.91	1.65	7.35	1.64
2048	10.42	2.22	11.33	1.81

Potassium Sulphocyanate, KCNS

The mother solution was prepared by direct weighing.

Table XLVII.—Molecular Conductivity and Dissociation

V	35°		50°		65°	
	μ_v	α	μ_v	α	μ_v	α
4	127.6	79.2	160.2	77.6	191.1	76.2
8	132.9	82.4	166.7	80.8	201.8	80.4
32	142.3	88.3	179.6	87.0	219.6	87.5
128	149.3	92.6	190.0	92.1	232.4	92.6
512	153.7	95.4	192.6	93.3	239.3	95.4
2048	161.2	100.0	206.4	100.0	250.9	100.0

Table XLVIII.—Temperature Coefficients

V	35°–50°		50°–65°	
	Cond. units	Per cent.	Cond. units	Per cent.
4	2.17	1.70	2.06	1.29
8	2.25	1.69	2.34	1.40
32	2.49	1.75	2.67	1.49
128	2.74	1.84	2.83	1.49
512	2.60	1.69	3.11	1.62
2048	3.01	1.86	2.97	1.44

Monopotassium Phosphate, H_2KPO_4

The mother solution was standardized by determining phosphoric acid as magnesium pyrophosphate.

Table XLIX.—Molecular Conductivity and Dissociation

V	35°		50°		65°	
	μ_v	α	μ_v	α	μ_v	α
8	310.4	63.8	391.6	64.5	477.2	61.2
32	380.0	78.1	481.2	79.2	588.4	75.5
128	424.3	87.2	537.6	88.5	661.2	84.8
512	452.3	93.0	573.1	94.4	708.2	90.9
2048	471.5	96.9	599.9	98.8	740.9	95.1
8192	486.4	100.0	621.4	100.0	779.4	100.0

Table L.—Temperature Coefficients

V	35°–50°		50°–65°	
	Cond. units	Per cent.	Cond. units	Per cent.
8	5.41	1.74	5.71	1.46
32	6.75	1.78	7.15	1.49
128	7.55	1.78	8.24	1.53
512	8.05	1.78	9.01	1.57
2048	8.56	1.81	9.40	1.58
8192	9.00	1.82	10.53	1.69

Potassium Acetate, $\text{KC}_2\text{H}_3\text{O}_2$

The mother solution was standardized by determining potassium as the sulphate.

Table LI.—Molecular Conductivity and Dissociation

V	35°		50°		65°	
	μ_v	α	μ_v	α	μ_v	α
4	94.4	75.40	125.6	78.84	142.1	72.13
8	102.7	82.03	131.6	82.61	160.4	81.42
32	112.0	89.46	147.0	92.28	180.8	91.78
128	118.7	94.81	154.6	97.05	184.5	93.66
512	125.2	100.00	159.3	100.00	194.9	98.94
2048	123.3		157.7		197.0	100.00

Table LII.—Temperature Coefficients

V	35°-50°		50°-65°	
	Cond. units	Per cent.	Cond. units	Per cent.
4	2.08	2.20	1.10	0.88
8	1.93	1.88	1.92	1.46
32	2.33	2.08	2.25	1.53
128	2.40	2.02	2.00	1.29
512	2.27	1.81	2.37	1.49
2048	2.29	1.86	2.62	1.66

Calcium Chloride, CaCl₂.6H₂O

The mother solution was standardized by determining calcium as carbonate and chlorine by Mohr's method.

Table LIII.—Molecular Conductivity and Dissociation

V	35°		50°		65°	
	μ_v	α	μ_v	α	μ_v	α
4	189.1	63.41	237.7	62.22	290.4	61.16
8	208.1	69.78	258.5	67.67	318.7	67.12
32	242.0	81.15	306.5	80.24	378.5	79.72
128	267.1	89.57	340.8	89.21	418.9	88.22
512	283.5	95.07	362.4	94.87	452.5	95.30
2048	298.2	100.0	382.0	100.00	474.8	100.00

Table LIV.—Temperature Coefficients

V	35°-50°		50°-65°	
	Cond. units	Per cent.	Cond. units	Per cent.
4	3.24	1.71	3.51	1.48
8	3.36	1.62	4.01	1.55
32	4.30	1.78	4.80	1.57
128	4.91	1.84	5.21	1.53
512	5.26	1.86	6.01	1.66
2048	5.59	1.88	6.19	1.62

Magnesium Chloride, MgCl₂.6H₂O

The mother solution was standardized by determining magnesium as magnesium pyrophosphate and chlorine by Mohr's method.

Table LV.—Molecular Conductivity and Dissociation

V	35°		50°		65°	
	μ_v	α	μ_v	α	μ_v	α
4	179.8	62.17	228.0	61.09	280.6	60.27
8	196.5	67.95	249.7	66.91	303.8	65.25
32	231.6	80.08	294.7	78.97	364.8	78.35
128	249.8	86.37	311.8	83.55	401.6	86.25
512	269.9	91.20	348.3	93.33	433.1	93.02
2048	289.2	100.00	373.2	100.00	465.6	100.00

Table LVI.—Temperature Coefficients

V	35°–50°		50°–65°	
	Cond. units	Per cent.	Cond. units	Per cent.
4	3.21	1.79	3.51	1.54
8	3.55	1.81	3.61	1.45
32	4.21	1.82	4.67	1.58
128	4.13	1.65	5.93	1.90
512	5.23	1.94	5.65	1.62
2048	5.60	1.94	6.16	1.65

Manganese Sulphate, MnSO₄·4H₂O

The mother solution was standardized by determining manganese as manganous pyrophosphate and sulphuric acid as barium sulphate.

Table LVII.—Molecular Conductivity

V	35°	50°	65°
4	78.0	88.0	108.3
8	92.6	112.8	130.0
32	128.5	156.4	181.8
128	166.7	204.1	241.9
512	219.4	277.5	338.7
2048	246.0	326.7	404.6

Table LVIII.—Temperature Coefficients

V	35°–50°		50°–65°	
	Cond. units	Per cent.	Cond. units	Per cent.
4	0.67	0.86	1.35	1.53
8	1.35	1.46	1.15	1.04
32	1.86	1.45	1.69	1.08
128	2.49	1.49	2.52	1.24
512	3.87	1.76	4.08	1.47
2048	5.38	2.19	5.19	1.59

Ferric Chloride, FeCl₃.6H₂O

The mother solution was standardized by determining iron as ferric oxide.

Table LIX.—Molecular Conductivity and Dissociation

V	35°		50°		65°	
	μ_v	α	μ_v	α	μ_v	α
4	214.3	16.92	269.5	17.71	327.0	19.39
8	276.5	21.83	346.9	23.32		
32	424.7	33.52	515.8	34.68		
128	827.1	65.29	1037.6	69.75	1512.5	89.71
512	1050.7	82.94	1405.4	94.48	1685.9	100.00
2048	1266.8	100.00	1487.5	100.00	1673.6	

Table LX.—Temperature Coefficients

V	35°–50°		50°–65°	
	Cond. units	Per cent.	Cond. units	Per cent.
4	3.68	1.72	3.83	1.42
8	4.69	1.70		
32	6.07	1.43		
128	14.00	1.69	31.7	3.85
512	23.6	2.25	18.7	1.33
2048	14.7	1.60	12.4	0.83

Chromium Sulphate (Green Variety)

The mother solution was standardized by determining chromium as chromic oxide.

Table LXI.—Molecular Conductivity

V	35°	50°	65°
4	128.2	160.0	189.6
8	183.5	227.8	262.9
32	302.0	354.4	417.4
128	433.9	522.7	606.0
512	673.3	811.1	977.3
2048	961.1	1207.8	1534.7

Table LXII.—Temperature Coefficients

V	35°–50°		50°–65°	
	Cond. units	Per cent.	Cond. units	Per cent.
4	2.12	1.65	1.97	1.23
8	2.95	1.61	2.34	1.03
32	3.49	1.16	4.20	1.19
128	5.92	1.34	5.55	1.06
512	9.19	1.37	11.08	1.37
2048	16.45	1.71	21.79	1.80

Nickel Nitrate, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$

The mother solution was standardized by determining nickel as nickel oxide.

Table LXIII.—Molecular Conductivity and Dissociation

V	35°		50°		65°	
	μ_2	α	μ_2	α	μ_2	α
4	200.8	61.0	252.4	60.1	306.6	59.4
8	216.8	65.8	276.3	65.6	343.5	66.6
32	260.1	79.0	330.3	78.6	402.4	78.0
128	289.7	89.8	369.2	87.9	453.2	87.8
512	314.2	95.4	399.7	95.2	494.8	95.9
2048	329.3	100.0	420.0	100.0	516.0	100.0

Table LXIV.—Temperature Coefficients

V	35°–50°		50°–65°	
	Cond. units	Per cent.	Cond. units	Per cent.
4	3.44	1.71	3.61	1.43
8	3.97	1.83	4.48	1.62
32	4.68	1.80	4.81	1.46
128	5.30	1.83	5.60	1.52
512	5.70	1.81	6.34	1.59
2048	6.05	1.84	6.40	1.52

Nickel Sulphate, $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$

The mother solution was standardized by determining sulphuric acid as barium sulphate.

Table LXV.—Molecular Conductivity

V	35°	50°	65°
4	78.6	95.5	111.8
8	93.1	115.5	135.7
32	127.0	158.2	187.8
128	171.8	215.6	259.8
512	219.4	278.9	339.7
2048	264.0	341.3	425.7

Table LXVI.—Temperature Coefficients

V	35°–50°		50°–65°	
	Cond. units	Per cent.	Cond. units	Per cent.
4	1.13	1.44	1.09	1.14
8	1.49	1.60	1.35	1.17
32	2.08	1.64	1.97	1.25
128	2.92	1.70	2.95	1.37
512	3.97	1.81	4.05	1.45
2048	5.15	1.95	5.63	1.65

Cobalt Sulphate, CoSO₄.7H₂O

The mother solution was standardized by determining sulphuric acid as barium sulphate.

Table LXVII.—Molecular Conductivity

V	35°	50°	65°
4	80.0	95.6	112.7
8	94.9	117.2	137.5
32	129.1	160.0	189.6
128	172.5	203.4	256.6
512	229.8	290.7	346.0
2048	264.8	340.3	421.6

Table LXVIII.—Temperature Coefficients

V	35°-50°		50°-65°	
	Cond. units	Per cent.	Cond. units	Per cent.
4	1.04	1.30	1.14	1.19
8	1.49	1.57	1.35	1.15
32	2.06	1.59	1.97	1.23
128	2.06	1.19	3.55	1.74
512	4.06	1.76	3.49	1.20
2048	5.03	1.90	5.42	1.59

Copper Sulphate, CuSO₄.5H₂O

The mother solution was standardized by determining copper as copper oxide and sulphuric acid as barium sulphate.

Table LXIX.—Molecular Conductivity

V	35°	50°	65°
4	75.6	93.8	107.4
8	90.5	109.1	124.5
32	126.1	152.7	173.8
128	170.7	210.3	247.3
512	222.7	279.1	337.7
2048	266.3	343.3	422.7

Table LXX.—Temperature Coefficients

V	35°-50°		50°-65°	
	Cond. units	Per cent.	Cond. units	Per cent.
4	1.21	1.60	0.91	0.97
8	1.24	1.37	1.02	0.93
32	1.77	1.40	1.41	0.92
128	2.64	1.55	2.45	1.16
512	3.76	1.69	3.91	1.40
2048	5.13	1.93	5.29	1.54

DISCUSSION OF RESULTS

Salts Studied from 0° to 35°

The conductivity data (Tables XXIV to XXXVIII) for the salts derived from diacid bases are of the same general character. This is best seen by drawing curves. Fig. I shows

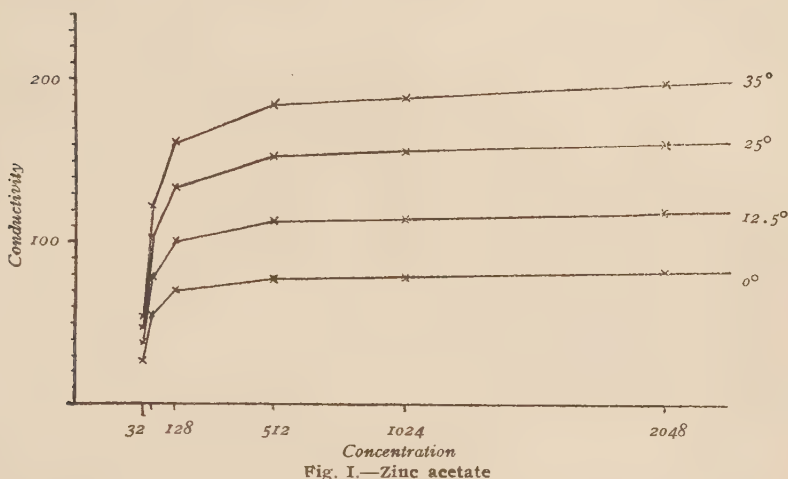


Fig. I.—Zinc acetate

conductivity-concentration curves for zinc acetate, which may be taken as an example of these salts. The diagrams for the other members of the group are similar, except that the curve is much flattened in the cases of lead acetate and calcium chromate. This is apparent in Fig. II, which gives the conductivity-concentration curves for lead acetate.

Lead acetate presents a number of exceptions. In concentrated solutions it has the smallest molecular conductivity and dissociation of any of the salts studied. At infinite dilution, however, the conductivity is nearly the same at all temperatures as for zinc acetate. Again, lead acetate shows the smallest temperature coefficients of conductivity at high temperatures, and the most rapid increase with dilution of any of the salts brought within the scope of this investigation.

It has been known that dissociation seems to be nearly independent of temperature over the range of temperature at

which my work was done, but in general decreases as the temperature rises. This is true of all but four of the salts included in this investigation.

The four apparent exceptions are potassium acetate, calcium formate, lead acetate and sodium ferrocyanide. Potassium acetate shows no well-marked change in the dissociation with temperature. Dissociation apparently increases as the temperature rises in the cases of calcium formate and sodium ferrocyanide. The same is true of lead acetate in concentrated solutions. It is intended to study farther the dissociation of these apparently exceptional salts.

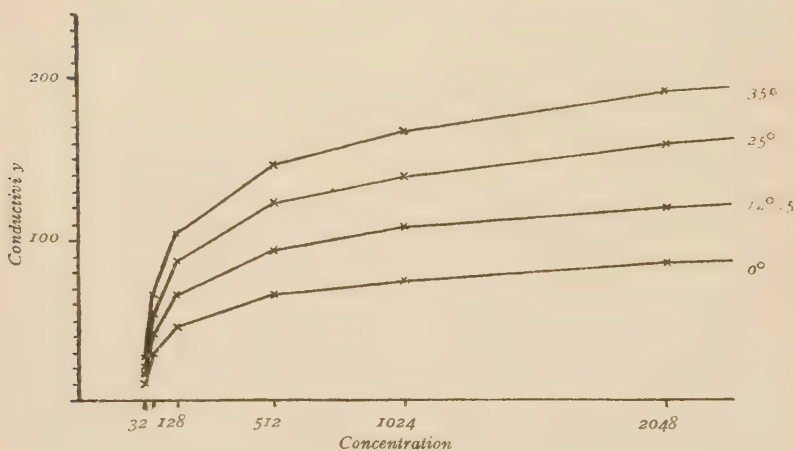


Fig. II.—Lead acetate

The complex salt sodium ferrocyanide has high conductivity and large temperature coefficients of conductivity. The percentage coefficients are remarkably constant at the various dilutions. The value for μ_{∞} was hardly reached at the highest dilution used, which is probably due, in part at least, to the breaking down into simpler ions in the more dilute solutions. Hydrolysis also probably takes place.

The remaining salts studied over the lower range in temperature are double salts and all are sulphates. Ammonium copper sulphate and potassium nickel sulphate yield very similar conductivity data. In the stronger solutions the

nickel salt shows the greater conductivity, but at higher dilution the molecular conductivity and the temperature coefficients of these two salts are almost identical. Conductivity in these cases is probably somewhat affected by hydrolysis.

A comparison of the data for the violet and green varieties of ammonium chrome alum shows that in the more concentrated solutions the green variety has much higher conductivity. At higher dilutions the reverse is true; the violet conducts better than the green form. The same general relation is shown in the case of potassium chrome alum, though μ_v for the green variety does not actually fall below the μ_v value for the violet form at the highest dilution employed. This relation between the two varieties appears in Fig. III.

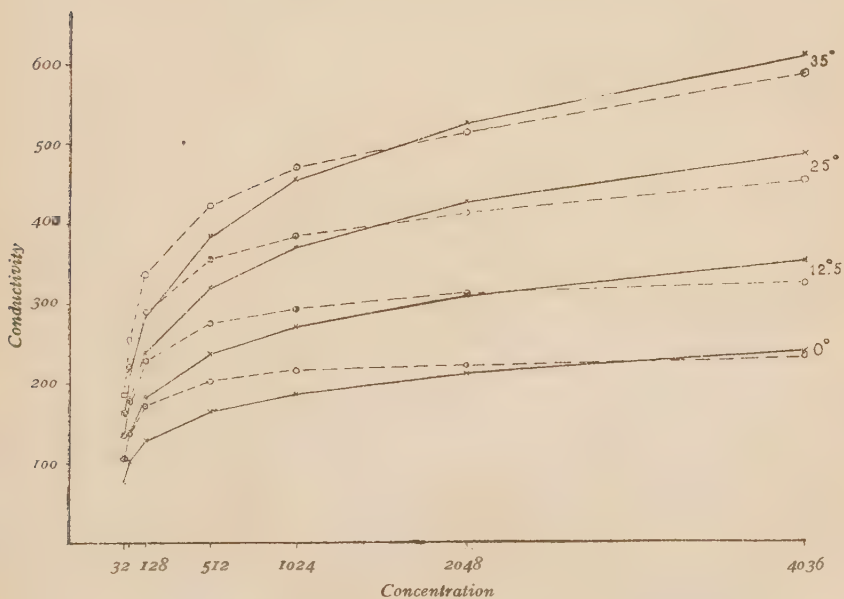


Fig. III.—Ammonium chromium sulphate { —x—x—x— Violet variety
 --(•)--(•)--(•)-- Green variety

The violet form of the chromium salts is transformed into the green variety by heating the solid salt or its solution for some time at about 70°. The relation between the two forms

has been the subject of many investigations. Monti¹ observed that the change was accompanied by an increase in the conductivity of the solution. Recoura,² in an elaborate investigation, explained the change as hydrolytic, resulting in the formation of free sulphuric acid and a basic salt. This conclusion was confirmed by Whitney.³ Jones and Mackay⁴ showed by conductivity measurements that the transformation was continuous as the temperature rose slowly from 37°.5 to 90°.

In the light of the conclusions of these workers, the explanation of the relative conductivity of the two forms of ammonium chrome alum would seem to be that the green modification, by virtue of the hydrolysis caused by heating, has the higher initial conductivity, but when diluted it is incapable of further hydrolysis to the same extent as appears to occur in the case of the normal violet variety.

Salts Studied from 35° to 65°

Before considering in detail the salts studied from 35° to 65° some general relations should be discussed. It was found by Jones and Ota⁵ and by Jones and Knight⁶ that concentrated solutions of certain salts in water often show abnormally great depressions of the freezing point of the solvent. It was also shown to be true in many cases that the molecular lowering of the freezing point increased from a certain concentration both with dilution and with increased concentration. The subject was further studied by Jones and Chambers⁷ and by Jones and Getman.⁸ It was found that the molecular conductivities of solutions of the substances which showed a minimum in the value of the molecular lowering were perfectly normal at all concentrations.

¹ Z. anorg. Chem., **12**, 75 (1896).

² Ann. chim. phys., [7] **4**, 494 (1895).

³ Z. physik. Chem., **20**, 40 (1896).

⁴ Am. Chem. J., **19**, 103 (1897).

⁵ *Ibid.*, **22**, 5 (1899).

⁶ *Ibid.*, **22**, 110 (1899).

⁷ *Ibid.*, **23**, 89 (1900).

⁸ Z. physik. Chem., **40**, 244 (1903).

To account for the facts, Jones¹ offered the suggestion that the molecules of the dissolved substance form complex compounds or hydrates with a portion of the water, thus virtually increasing the concentration of the solution. The freezing point is thus abnormally depressed. It was also pointed out that substances which give these abnormal results are often hygroscopic and that, when dehydrated, they readily combine with water. Jones and his assistants have collected a large amount of evidence,² by several independent methods, which supports the theory of hydration. A method³ was developed by which the approximate composition of the hydrates of many substances was calculated.

It was pointed out by Jones⁴ that the breaking down of the hydrated molecules, or of the hydrated ions, by a rise in temperature would diminish the mass of the ion and thus increase the conductivity. The more complex the hydrates the greater would be the change in hydration and, consequently, the greater the change in conductivity. Therefore "we should expect to find *those ions with the largest hydrating power having the largest temperature coefficients of conductivity.*"⁵ An examination of the experimental results of Jones and West⁶ led to the following conclusions:

1. The temperature coefficients of conductivity of aqueous solutions of electrolytes are greater, the greater the hydrating power of the electrolyte.
2. The temperature coefficients of conductivity of aqueous solutions of electrolytes are of the same order of magnitude for those substances having, approximately, the same hydrating power.
3. The temperature coefficients of conductivity, for any given substance, increase with the dilution of the solution, and the increase is greatest for those substances with large hydrating power.⁷

¹ Am. Chem. J., **23**, 103 (1900).

² See Hydrates in Aqueous Solution; Carnegie Institution of Washington, Publication No. 60.

³ *Ibid.*, pp. 28-145.

⁴ Am. Chem. J., **35**, 445 (1906).

⁵ *Loc. cit.*, p. 447.

⁶ Am. Chem. J., **34**, 357 (1905).

⁷ *Ibid.*, **35**, 450 (1906).

Similar results were obtained by Jones and Clover.¹

The composition of the hydrates formed by some of the substances which were brought within the scope of this investigation has been approximately determined by Jones² and his assistants. In general, the hydrating power may be taken as roughly proportional to the amount of water of crystallization.

The substances named in Table LXXI crystallize with little or no water, and have slight hydrating power. They are seen to have small temperature coefficients of conductivity. The substances named in Table LXXII have large hydrating power and also have large temperature coefficients of conductivity.

Table LXXI.—Substances with Slight Hydrating Power

	Temperature coefficients in conductivity units				
	V		V		Temp. range
KCNS	4	2.17	2048	3.01	35°–50°
KC ₂ H ₃ O ₂	4	2.08	2048	2.29	35°–50°
Ca(OOCH) ₂	4	2.15	2048	4.02	25°–35°
Zn(C ₂ H ₃ O ₂) ₂	4	0.70	2048	3.69	25°–35°
Pb(C ₂ H ₃ O ₂) ₂ ·3H ₂ O	4	0.49	2048	3.23	25°–35°
CaCrO ₄ ·2H ₂ O	8	1.96	2048	5.00	25°–35°

Table LXXII.—Substances with Large Hydrating Power

	Temperature coefficients in conductivity units				
	V		V		Temp. range
Ni(NO ₃) ₂ ·6H ₂ O	4	3.44	2048	6.05	35°–50°
CaCl ₂ ·6H ₂ O	4	3.24	2048	5.59	35°–50°
MgCl ₂ ·6H ₂ O	4	3.21	2048	5.60	35°–50°
Zn(NO ₃) ₂ ·6H ₂ O	4	2.46	2048	4.78	25°–35°
FeCl ₃ ·6H ₂ O	4	3.68	2048	14.7	35°–50°
HNa ₂ PO ₄ ·12H ₂ O	8	2.82	2048	4.65	35°–50°
H ₂ KPO ₄	8	5.41	2048	8.56	35°–50°
Na ₂ B ₄ O ₇ ·5H ₂ O	16	2.77	2048	4.73	35°–50°

The values used in these tables are not strictly comparable, since the concentrations and the ranges of temperatures at which the temperature coefficients were determined are not the same throughout, but the agreement is sufficiently close to warrant their use in showing the general relations.

¹ Am. Chem. J., **43**, 215 (1906).

² Hydrates in Aqueous Solution; Carnegie Institution of Washington, No. **60**.

My results confirm the conclusion of Jones cited above, and are in perfect accord with the theory of hydration advanced by him.

The sulphates which I have studied in this investigation are omitted from Tables LXXI and LXXII, because, as shown by Jones and his coworkers,¹ the sulphates usually show abnormal results. In general, sulphates have very small temperature coefficients of conductivity, and appear to have small hydrating power in solution. There is evidence that some sulphates, at least, are polymerized in concentrated solutions.

Sodium tetraborate gives normal conductivity results at 35°, but at higher temperatures the increase in conductivity with dilution is exceptionally rapid. The salt also has large temperature coefficients of conductivity, and is undoubtedly hydrated in solution. Boric acid being little dissociated and, therefore, a weak acid, the sodium salt would certainly undergo hydrolysis. By assuming both hydration and hydrolysis to take place, the behavior of the salt is easily accounted for. At the lower temperatures the hydrolysis, due to increasing dilution, is balanced by the increasing complexity of the fairly stable hydrates. As the temperature rises the hydrates break down, while hydrolysis continues unchecked so that the conductivity increases rapidly.

Calcium and magnesium chlorides give almost identical results, except that the molecular conductivity of the calcium salt is about ten conductivity units above that of magnesium chloride. The latter salt shows greater increase in the value of μ_v with dilution at 56°, which accords with its greater hydration, as shown by Jones and Bassett.²

Nickel nitrate also shows large temperature coefficients. It is known³ to possess marked power of hydration.

The conductivity data for the sulphates of nickel, cobalt, copper, and manganese are remarkably similar in every re-

¹ Hydrates in Aqueous Solution; Carnegie Institution of Washington, Publication No. 60, pp. 80, 136, 148.

² Am. Chem. J., 33, 555 (1905).

³ Jones: Hydrates in Aqueous Solution; Carnegie Institution of Washington, Publication No. 60, p. 78.

spect. There is little indication of an approach to μ_{∞} at the highest dilution employed. The temperature coefficients are not large in concentrated solutions, but increase rapidly with dilution. This behavior is probably due, in part at least, to the polymerization of the sulphates in concentrated solutions.

The molecular conductivity of the quaternary electrolytes, chromium sulphate and ferric chloride, increases very rapidly with dilution and also, in dilute solutions, with rise in temperature. Hydrolysis undoubtedly plays a prominent part. In the case of ferric chloride distinct precipitation, due to hydrolysis, occurred at 65° in the N/8 and N/32 solutions. The conductivity curve of this salt is interesting (Fig. IV).

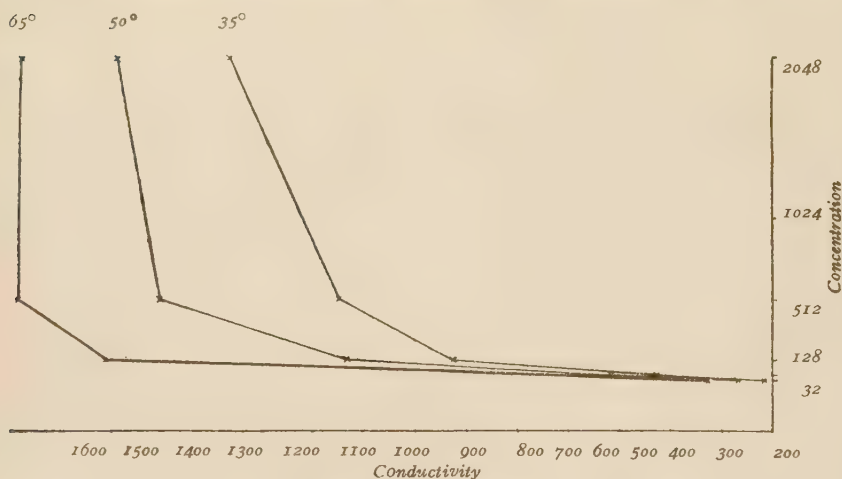
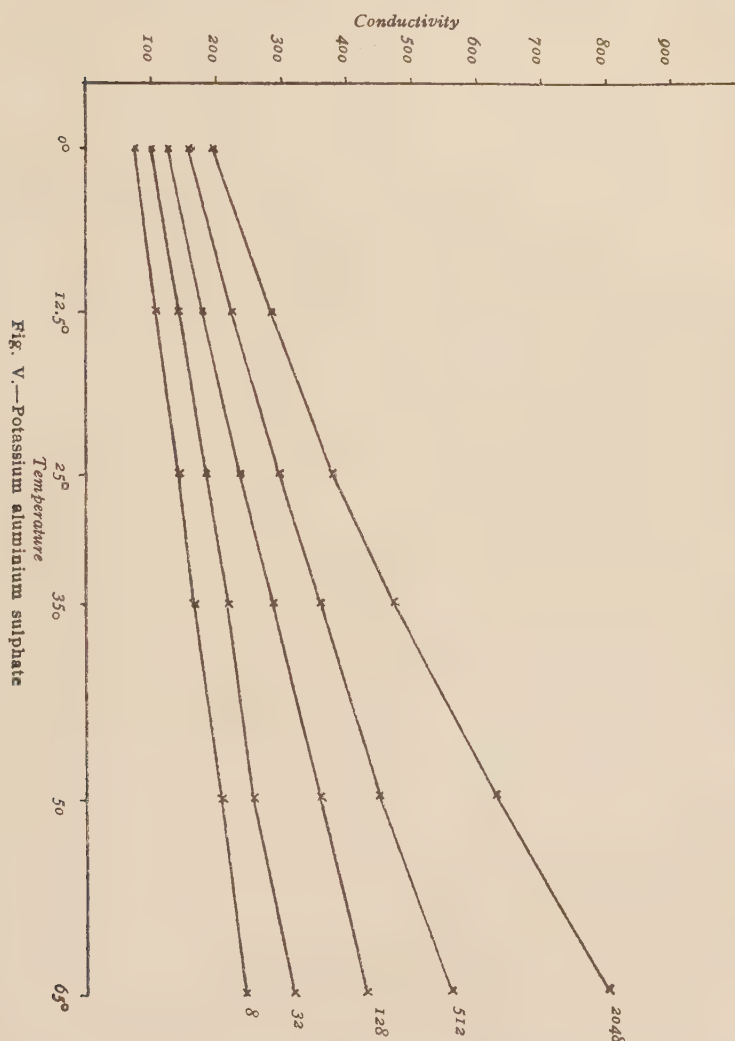


Fig. IV.—Ferric chloride

The abrupt bend in the curve for 50° and 65° at the N/512 concentration indicates that the cause of the increasing conductivity—presumably hydrolysis—is rapidly becoming less effective. It would seem that under these conditions of temperature and dilution the hydrolysis of the salt is very great.

The ammonium and potassium alums were studied through both ranges of temperature (0° – 35° and 35° – 65°), and the

values of μ_v recorded for 35° were deduced from all the readings made at this temperature. Fig. V shows the conduc-



tivity-temperature curves for potassium alum through the entire range of temperature. In strong solutions, at ordinary

temperatures, molecular conductivity is nearly a linear function of temperature; but at greater dilutions the curve is parabolic.¹ All of the salts studied in this investigation yield conductivity-temperature curves of this same general character.

The condition of double salts, when in solution, presents a problem of interest. Investigators have sought for evidence which would decide whether such salts, when dissolved, break down into their constituent salts, which then dissociate in the usual way; or whether they ionize to some extent as salts of complex acids. Four investigations² bearing on the general problem have been carried out in this laboratory. Jones and Mackay compared the conductivity of certain alums with the sum of the conductivities of the constituent salts. They found the conductivity of the alums in dilute solutions to be almost the same as the sum of the conductivities of the components. In concentrated solutions the alums were found to have a conductivity less than the sum of the conductivities of the components, and the difference increased with the concentration. The difference was greater than that observed when mixtures of sulphates incapable of forming double salts were compared. Similar methods were used by the other workers. The general conclusion from these researches was that the double salts in moderately concentrated solutions are not wholly broken down into the simple salts.

In these investigations the conductivities were measured at 25°. As we now have at hand conductivity data over a considerable range in temperature, it appears to be of interest to apply the method of Jones and Mackay at other temperatures.

The following is the table of Jones and Mackay³ giving the comparisons for potassium alum at 25°:

¹ Jones and Jacobson: *Am. Chem. J.*, **40**, 402 (1908). White and Jones: *Ibid.*, **44**, 199 (1910).

² Jones and Mackay: *Ibid.*, **19**, 83 (1897). Jones and Ota: *Ibid.*, **22**, 5 (1899). Jones and Knight: *Ibid.*, **22**, 110 (1899). Jones and Caldwell: *Ibid.*, **25**, 349 (1901).

³ *Ibid.*, **34**, 357 (1905).

Table LXXIII.—Potassium Alum, 25° (Jones and Mackay)

V	K ₂ SO ₄	Al ₂ (SO ₄) ₃	Sum/2	KAlSO ₄	Diff. Per cent.
5	172.7	108.0	140.3	133.9	—4.5
8	183.3	124.2	153.7	149.2	—3.0
20	205.1	158.1	181.6	178.3	—1.7
40	220.3	185.7	203.0	202.5	—0.2
200	252.4	290.4	271.4	269.0	—0.8
400	262.2	342.6	302.4	305.2	+0.9

This may be compared with Table LXXIV, which gives the corresponding relations at 0°, 35°, and 65°. The values of the conductivity of aluminum sulphate were kindly furnished by Miss L. G. Winston. The conductivity values of potassium sulphate are taken from the work of Jones and West.¹

Table LXXIV.—Potassium Alum

0°						
V	K ₂ SO	Al ₂ (SO ₄) ₃	Sum/2	KAlSO ₄	Diff.	Diff. Per cent.
8	101.9	65.2	83.6	78.9	—4.7	—5.6
32	117.9	89.5	103.7	101.2	—2.5	—2.4
128	131.9	121.8	126.9	127.6	+0.7	+0.5
512	142.7	164.1	153.4	158.8	+5.4	+3.5
35°						
8	220.3	137.2	178.8	165.3	—13.5	—7.5
32	259.7	197.1	228.4	215.7	—12.7	—5.5
128	296.9	274.1	285.5	283.7	—1.8	—0.6
512	319.6	388.1	353.9	358.3	+4.4	+1.2
65°						
8	332.8	188.4	260.6	240.6	—20.0	—7.7
32	400.0	264.6	332.3	317.4	—14.9	—4.5
218	456.2	387.6	421.9	426.2	+4.3	+1.0
512	500.7	581.6	541.1	557.1	+16.0	+2.9

My values for "difference" in per cent. are of the same order of magnitude as those obtained by Jones and Mackay, and confirm their conclusions. It is noticeable that the percentage differences are nearly the same at the various temperatures. This may be regarded as evidence that the breaking down of potassium alum in solution is little affected by temperature, which, from other evidence, is known to be true of dissociation in general.

¹ Am. Chem. J., **34**, 357 (1905).

In Table LXXV, from the work of Jones and Caldwell,¹ the conductivity of the double salt, potassium nickel sulphate, is compared with the sum of the conductivities of the components, all measurements being made at 25°. Table LXXVI shows the same relations for this salt at 0° and 35°. The values for the conductivity of nickel sulphate given in Table LXXVI are taken from the work of Jones and Jacobson.²

Table LXXV.—Potassium Nickel Sulphate, 25° (Jones and Caldwell)

V	K ₂ SO ₄	NiSO ₄	Sum	K ₂ Ni(SO ₄) ₂	Diff.	Diff. Per cent.
8	182.4	77.9	260.3	219.5	—40.8	—15.6
40	220.3	109.0	329.3	291.6	—37.7	—11.4
80	237.9	122.8	360.7	323.7	—37.0	—10.3
400	262.2	173.1	435.3	400.2	—35.1	—8.0
800	273.0	194.8	467.8	438.0	—29.0	—6.2

Table LXXVI.—Potassium Nickel Sulphate

0°						
V	K ₂ SO ₄	NiSO ₄	Sum	K ₂ Ni(SO ₄) ₂	Diff.	Diff. Per cent.
8	101.9	40.4	142.3	122.6	—19.7	—13.8
32	117.9	54.8	172.7	155.4	—17.3	—10.0
128	131.9	73.9	205.8	187.5	—18.3	—8.9
512	142.7	93.1	235.8	219.6	—16.2	—6.9
1024	145.0	100.4	245.4	235.5	—9.9	—4.0
35°						
8	219.8	90.9	310.7	268.3	—42.4	—13.7
32	256.9	123.0	379.9	339.7	—40.2	—10.6
128	291.0	168.4	459.4	414.1	—45.3	—9.8
512	318.4	213.5	531.9	490.7	—41.2	—7.7
1024	325.0	234.6	559.6	527.1	—32.5	—5.8

The percentage "differences" at 0° and 35° agree closely with those found by Jones and Caldwell at 25°, showing that the relations which they established as holding at 25° are also true at higher and lower temperatures. My results also accord with the general law that dissociation is nearly independent of temperature.

¹ Am. Chem. J., **25**, 349 (1901).

² *Ibid.*, **40**, 390 (1908).

SUMMARY

1. The molecular conductivities of fifteen inorganic salts from 0° to 35° , and of sixteen inorganic salts from 35° to 65° , were measured by the Kohlrausch method. The temperature coefficients of conductivity, both in conductivity units and in percentages, were calculated for these salts through the ranges of temperature above stated. The percentage dissociations were also calculated in all cases where the data were sufficient.

2. Jones and his coworkers¹ have shown that the ions of an electrolyte are hydrated in aqueous solutions, and that the complexes break down with rise in temperature, thus increasing the conductivity. If this is true, substances of large hydrating power should have large temperature coefficients of conductivity. Jones² showed this to be true for the substances studied by Jones and West.³ The substances which I have studied show the same relations and my results are in perfect accord with the theory of hydration.

3. Hydrolysis is evidently a frequent cause of abnormally great conductivity. It is increased both by dilution and by rise in temperature.

4. Another probable cause of abnormally rapid increase in conductivity is decrease in polymerization. There is evidence that sulphates are polymerized in concentrated solutions.

5. Observers have found an increase in the conductivity of a solution of a chromium salt when it is changed from the violet to the green variety. My results show that while the conductivity is increased in concentrated solutions by this change, the increase is relatively less at higher dilutions. The conductivity of the green variety may even fall below that of the violet variety. This would appear to show that the green variety is not as susceptible to hydrolysis by dilution as is the normal violet form.

¹ Hydrates in Aqueous Solution; Carnegie Institution of Washington, Publication No. 80.

² *Am. Chem. J.*, **35**, 445 (1906).

³ *Ibid.*, **34**, 357 (1905).

6. Jones and his coworkers¹ found that the conductivities of alums and other double salts were less than the sum of the conductivities of the constituent salts. They inferred that double salts exist as such to some extent in concentrated solutions. Their work was done at 25°. I have made similar comparisons at other temperatures, and find that the relations pointed out by them as holding at 25° also manifest themselves from 0° to 65°. In addition, my results show that the breaking down or dissociation of double salts, like dissociation in general, is little affected by temperature.

The following general relations, established by previous investigators, are true of the salts which I have studied:

7. The temperature-conductivity curves for concentrated solutions are nearly straight lines; at higher dilutions the curves are often parabolic.

8. The percentage temperature coefficients increase with dilution, but decrease with temperature. Temperature coefficients in conductivity units increase with dilution.

9. Dissociation decreases with temperature. Four salts among those studied seem to be exceptions to the rule.

¹ Jones and Mackay: *Am. Chem. J.*, **19**, 83 (1897). Jones and Ota: *Ibid.*, **22**, 5 (1899). Jones and Knight: *Ibid.*, **22**, 110 (1899). Jones and Caldwell: *Ibid.*, **25**, 349 (1901).

BIOGRAPHY.

Henry Hallock Hosford was born July 12, 1859, at Hudson, Ohio. He prepared for college at Hudson and entered Western Reserve College, graduating with the degree of Bachelor of Arts in 1880. Three years later he received the degree of Master of Arts from his Alma Mater.

After teaching for several years in Western Reserve Academy, Mr. Hosford became professor of chemistry in Doane College, Crete, Nebraska, which position he still occupies. In 1892 he married Jennie Chamberlain, daughter of Dr. W. I. Chamberlain, of Hudson, Ohio. They have four children.

In October, 1909, Mr. Hosford entered Johns Hopkins University as a graduate student in Chemistry with Physical Chemistry and Physics as his subordinate subjects.



